

Infrared spectroscopy of diatomic molecules - a fractional calculus approach

Richard Herrmann ^a

GigaHedron, Berliner Ring 80, D-63303 Dreieich, Germany

Received: September 11, 2012 / Accepted: September 11, 2012

Abstract. The eigenvalue spectrum of the fractional quantum harmonic oscillator is calculated numerically solving the fractional Schrödinger equation based on the Riemann and Caputo definition of a fractional derivative. The fractional approach allows a smooth transition between vibrational and rotational type spectra, which is shown to be an appropriate tool to analyze IR spectra of diatomic molecules.

PACS. 45.10.Hj Perturbation and fractional calculus methods – 33.15.Mt Rotation, vibration and vibration-rotation constants – 33.20.Ea Infrared spectra 31.15.X- Alternative approaches

1 Introduction

Besides Newton's *principia* Huygens treatise on the pendulum clock[1] may be considered as one of the most influential works in physics. Since then, the description of periodical motion in terms of the classical harmonic oscillator is a standard example for an exactly solvable problem in classical mechanics.

In non-relativistic quantum mechanics an arbitrary potential may be approximated using a harmonic expansion around the equilibrium position. Therefore it is the ideal tool to model vibrational degrees of freedom in many different quantum systems.

Consequently one of the first applications of the quantum harmonic oscillator was the analytic description of the vibrational energy contribution in quantum mechanical models of diatomic molecules [2].

To establish the standard model for a successful description of excitation spectra of diatomic molecules in addition to vibrations, rotational degrees of freedom have to be considered, so that the total energy of such a system is given in the simplest approximation mainly as a sum of both contributions (including e.g. anharmonic corrections and a rot-vib interaction term):

$$E_{\text{tot}} = E_{\text{vib}} + E_{\text{rot}} \quad (1)$$

It is the basic intention of this article, to propose an alternative approach based on fractional calculus, which overcomes the traditional distinction between rotational and vibrational degrees of freedom by introducing a more universal description, which treats rotations and vibrations simultaneously within the generalized framework of fractional oscillations.

The fractional calculus [3]-[5] provides a set of axioms and methods to extend the standard derivative definition in a reasonable way from integer order n to arbitrary order α :

$$\frac{\partial^n}{\partial x^n} \rightarrow \frac{\partial^\alpha}{\partial x^\alpha} \quad (2)$$

and therefore allows for an extended, smooth derivative definition, which may be used to determine generalized symmetries, which go beyond the $U(n)$ -symmetry of the standard harmonic oscillator.

In the following, we will first present the main results of a numerical solution of the fractional Schrödinger equation with the fractional harmonic oscillator potential.

We will then propose a fractional analogue to the standard rot-vib model used for a description of spectra of diatomic molecules. As a first application, we will use this model to describe the IR-spectrum of hydrogen chloride H^{35}Cl .

2 The fractional derivative

We will investigate the spectrum of the fractional quantum harmonic oscillator for two different definitions of the fractional derivative, namely the Riemann [6] and Caputo [7] fractional derivative. Both types are strongly related.

Starting with the definition of the fractional Riemann integral

$${}_R I^\alpha f(x) = \begin{cases} ({}_R I_+^\alpha f)(x) = \frac{1}{\Gamma(\alpha)} \int_0^x d\xi (x - \xi)^{\alpha-1} f(\xi) & x \geq 0 \\ ({}_R I_-^\alpha f)(x) = \frac{1}{\Gamma(\alpha)} \int_x^0 d\xi (\xi - x)^{\alpha-1} f(\xi) & x < 0 \end{cases} \quad (3)$$

the fractional Riemann derivative is defined as the product of a fractional integration followed by an ordinary differ-

^a email address: herrmann@gigahedron.com

entiation:

$${}_R\partial_x^\alpha = \frac{\partial}{\partial x} {}_R I^{1-\alpha} \quad (4)$$

The Caputo definition of a fractional derivative follows an inverted sequence of operations (4). An ordinary differentiation is followed by a fractional integration

$${}_C\partial_x^\alpha = {}_R I^{1-\alpha} \frac{\partial}{\partial x} \quad (5)$$

Applied to a function set $f(x) = x^{n\alpha}$ using the Riemann fractional derivative definition (4) we obtain:

$${}_R\partial_x^\alpha x^{n\alpha} = \frac{\Gamma(1+n\alpha)}{\Gamma(1+(n-1)\alpha)} x^{(n-1)\alpha} \quad x \geq 0 \quad (6)$$

while for the Caputo definition of the fractional derivative it follows for the same function set:

$${}_C\partial_x^\alpha x^{n\alpha} = \begin{cases} \frac{\Gamma(1+n\alpha)}{\Gamma(1+(n-1)\alpha)} x^{(n-1)\alpha} & n > 0 \\ 0 & n = 0 \end{cases} \quad x \geq 0 \quad (7)$$

Thus for e.g. polynomials with $x^{n\alpha}$ both derivative definitions only differ in the case $n = 0$.

3 Fractional quantum mechanics

The transition from classical mechanics to quantum mechanics may be interpreted as a transition from independent coordinate space and momentum space to a Hilbert space, in which space and momentum operators are treated similarly.

Consequently one postulate of quantum mechanics states, that derived results must be independent of the specific choice of e.g. a space or momentum representation. This is the mathematical manifestation of wave-particle-duality: A description in terms of either position \mathbf{x} or wave vector \mathbf{k} covers the properties of the same quantum object equivalently.

This implies, that a successful fractional extension of quantum mechanics has to treat coordinates and conjugated momenta equivalently:

$$\{x^n, \frac{d^n}{dx^n}\} \rightarrow \{x^\alpha, \frac{d^\alpha}{dx^\alpha}\} \quad x > 0 \quad (8)$$

This simultaneous treatment is the major difference between a classical and a quantum mechanical treatment. Furthermore this is the key information needed to quantize any classical quantity like a Hamilton function.

There are several different approaches, like canonical quantization [8], [9], path-integrals [10], Weyl phase-space quantization [11] or stochastic quantization [12].

To emphasize the equivalence between a space and a momentum representation, we will use the classical procedure, proposed by Dirac: The classical canonically conjugated observables x and p are replaced by a pair of quantum mechanical observables $\{\hat{x}, \hat{p}\}$, which are introduced

as derivative operators on a Hilbert space of square integrable wave functions f . The space representations of these operators are:

$$\hat{x}f(x) = xf(x) \quad (9)$$

$$\hat{p}f(x) = -i\hbar\partial_x f(x) \quad (10)$$

In order to extend this approach to the fractional case, we first make the following statement on parity conservation:

The parity properties of the standard coordinate x and derivative ∂_x should be conserved in the fractional case too. Therefore we postulate the following extensions valid on R :

$$\hat{x}^\alpha = \text{sign}(x)|x|^\alpha \quad (11)$$

$$\hat{D}_x^\alpha = \text{sign}(x) {}_{R,C}\partial_{|x|}^\alpha \quad (12)$$

and introduce the fractional pair $\{\hat{X}, \hat{P}\}$ of conjugated fractional derivative operators, which are given in space representation:

$$\hat{X}f(\hat{x}^\alpha) = \left(\frac{\hbar}{mc}\right)^{(1-\alpha)} \hat{x}^\alpha f(\hat{x}^\alpha) \quad (13)$$

$$\hat{P}f(\hat{x}^\alpha) = -i\left(\frac{\hbar}{mc}\right)^\alpha mc \hat{D}_x^\alpha f(\hat{x}^\alpha) \quad (14)$$

The attached factors $(\hbar/mc)^{(1-\alpha)}$ and $(\hbar/mc)^\alpha mc$ ensure correct length and momentum units. For the special case $\alpha = 1$ these definitions correspond to the classical limits (9) and (10).

With these operators, we may quantize the classical Hamilton function of the harmonic oscillator:

4 The fractional quantum harmonic oscillator

The classical Hamilton function of the harmonic oscillator is given by

$$H_{\text{class}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (15)$$

Following the canonical quantization procedure we replace the classical observables $\{x, p\}$ by the fractional derivative operators $\{\hat{X}, \hat{P}\}$ according to (13) and (14). The quantized Hamilton operator H^α results:

$$H^\alpha = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2 \hat{X}^2 \quad (16)$$

The stationary Schrödinger equation is given by

$$\begin{aligned} H^\alpha \Psi &= \\ &\left(-\frac{1}{2m} \left(\frac{\hbar}{mc}\right)^{2\alpha} m^2 c^2 \hat{D}_x^\alpha \hat{D}_x^\alpha + \frac{1}{2}m\omega^2 \left(\frac{\hbar}{mc}\right)^{2(1-\alpha)} |x|^{2\alpha}\right) \Psi \\ &= E' \Psi \end{aligned} \quad (17)$$

Introducing the variable ξ and the scaled energy E :

$$\xi^\alpha = \sqrt{\frac{m\omega}{\hbar}} \left(\frac{\hbar}{mc}\right)^{1-\alpha} x^\alpha \quad (18)$$

$$E' = \hbar\omega E \quad (19)$$

Table 1. Parameters in the ${}_{R,C}\Psi_n^\pm(\xi, \alpha)$ series expansion (24) and validity ranges of the fractional parameter α , which fulfills the requirement of normalizability of the wave function.

type	parity	τ	π	normalizable	$\Psi(\xi \approx 0)$
Riemann	even	$\alpha - 1$	0	$0.5 \leq \alpha \leq 2$	$o(\xi^{\alpha-1})$
Riemann	odd	$\alpha - 1$	α	$0.25 \leq \alpha \leq 2$	$o(\xi^{2\alpha-1})$
Caputo	even	0	0	$0 \leq \alpha \leq 2$	$o(\xi^0)$
Caputo	odd	0	α	$0 \leq \alpha \leq 2$	$o(\xi^\alpha)$

we obtain the stationary Schrödinger equation for the fractional harmonic oscillator in the canonical form

$$H^\alpha \Psi_n(\xi) = \frac{1}{2}(-\hat{D}_\xi^{2\alpha} + |\xi|^{2\alpha})\Psi_n(\xi) = E(n, \alpha)\Psi_n(\xi) \quad (20)$$

In contrast to the standard quantum harmonic oscillator this fractional Schrödinger equation has not been solved analytically until now.

An approximate solution for the energy levels has been derived by Laskin [13] within the framework of WKB-approximation, which is independent from a specific choice of a fractional derivative type:

$$E_{\text{WKB}}(n, \alpha) = \left(n + \frac{1}{2}\right)^\alpha \pi^{\alpha/2} \left(\frac{\alpha \Gamma(\frac{1+\alpha}{2\alpha})}{\Gamma(\frac{1}{2\alpha})}\right)^\alpha \quad n = 0, 1, 2, \dots \quad (21)$$

In a previous work [14] we have already emphasized, that these levels allow for a smooth transition from vibrational to rotational types of spectra, depending on the value of the fractional derivative coefficient α .

$$E_{\text{WKB}}(n, \alpha \approx 1) \sim n + \frac{1}{2} \quad n = 0, 1, 2, \dots \quad (22)$$

$$E_{\text{WKB}}(n, \alpha \approx 2) \sim (n + \frac{1}{2})^2 = n(n+1) + 1/4 \quad (23)$$

Therefore the fractional harmonic oscillator may be a useful tool to describe rot-vib spectra, with α in the range of $1 \leq \alpha \leq 2$. Consequently, the fractional harmonic oscillator could be of similar importance as its classical counterpart, an exact solution is of fundamental interest.

The main results from a numerical solution of the canonical Schrödinger equation of the fractional quantum harmonic oscillator (20) using the Riemann and Caputo fractional derivative definition are presented in the next section.

5 Numerical solution

For a numerical solution of (20), we expand the wave function in a fractional Taylor-series with good parity Π :

$${}_{R,C}\Psi_n^\pm(\xi, \alpha) = \xi^\tau \xi^\pi \sum_{i=0}^N a_i(E) \xi^{2\alpha i} \quad \xi > 0 \quad (24)$$

$$\Pi_{R,C}\Psi_n^\pm(\xi, \alpha) = \pm {}_{R,C}\Psi_n^\pm(\xi, \alpha) \quad (25)$$

where the parameters τ and π determining the type (Riemann or Caputo) of the fractional derivative definition

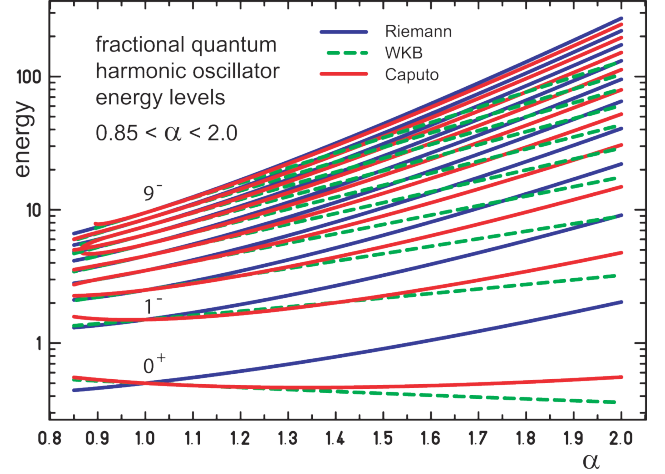


Fig. 1. Logarithmic plot of the first 10 energy levels of the fractional quantum harmonic oscillator in the range $0.85 \leq \alpha \leq 2$ based on the Riemann (blue), Caputo (red) and WKB-approximation (green) of the fractional derivative definition.

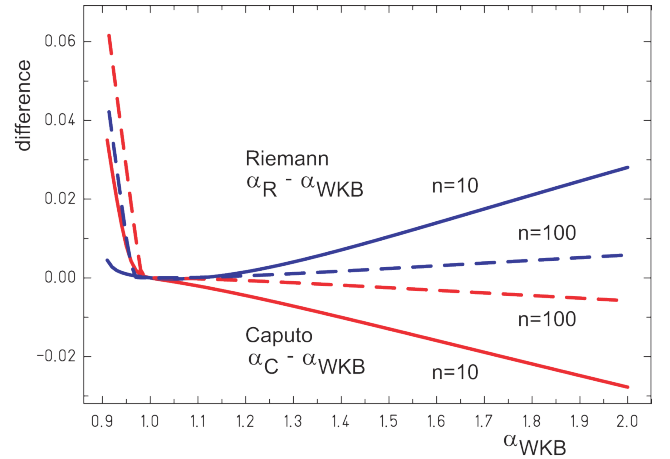


Fig. 2. Result of a least square fit of energy level spectra based on the Riemann (blue lines) and Caputo (red lines) derivative definition with the WKB-approximation (21). Plotted is the difference of α values for a given number of energy levels ($n = 10, 100$) with fitted α_{WKB} .

used and parity of the wave function are listed in table 1. The \pm index indicates the parity for n even and odd respectively.

The coefficients $a_i(E)$ are determined using a standard shooting method:

From the requirement, that the wave function should vanish at infinity for a given eigen value E_n follows a determining condition for sufficiently large distance ξ_{det} :

$$\lim_{E \rightarrow E_n} {}_{R,C}\Psi_n^\pm(\xi_{\text{det}}, \alpha, E) = 0 \quad (26)$$

which allows for an iterative procedure to calculate E_n with arbitrary precision.

For practical calculations, we determined the eigen values with a precision of 32 significant digits with the set-

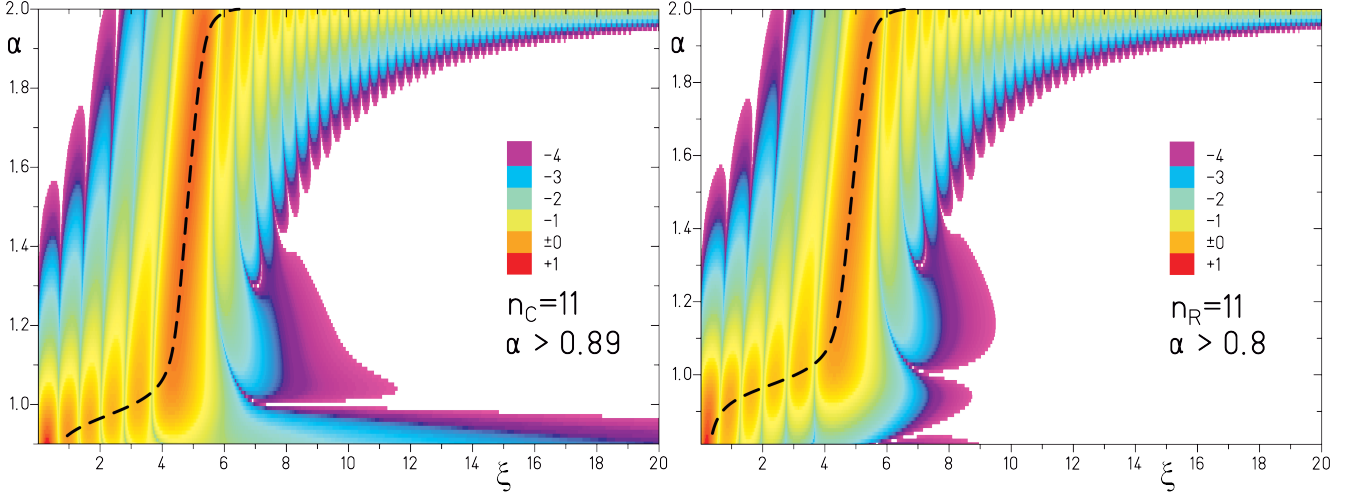


Fig. 3. Logarithmic probability density $|\Psi_{n=11}^-(\xi, \alpha)|^2$ for the solution of the fractional quantum harmonic oscillator based on the Caputo (left) and Riemann (right) definition of the fractional derivative in the full range of allowed α values for real energy eigenvalues. The dashed line indicates the expectation value for the modified position operator $\langle \bar{\xi} \rangle$.

tings $20 \leq \xi_{det} \leq 35$ and $1000 \leq N \leq 10000$, depending on α .

The major restriction for the range of allowed α values is the requirement of normalizability of the wavefunction obtained. From

$$\int_{-\infty}^{\infty} d\xi_{R,C} \Psi_n^{\pm}(\xi, \alpha) \xi_{R,C} \Psi_n^{\pm}(\xi, \alpha)^* < \infty \quad (27)$$

follows an upper bound $\alpha \leq 2$. Of course, for $\alpha > 2$ condition (26) may still be used as an equivalent of a box-normalization condition, but the results are no solutions of the harmonic oscillator potential any more.

In figure 1 we compare the resulting energy level spectra to the WKB-approximation. While in the vicinity of $\alpha = 1$ differences are negligible, for larger α values especially for low lying energies the calculated spectra differ significantly, but as a first remarkable result we obtain a smooth transition from vibrational to rotational type of spectrum using the Riemann and Caputo fractional derivative definition respectively.

The results of a fit of the energy levels with the WKB-approximation are plotted in figure 2. We may deduce, that for increasing number of energy levels n eq. (21) approximates the energy values better. From this figure we may also deduce, that rotational spectra, which are characterized by $\alpha_{WKB} = 2$ are reproduced using the Caputo derivative for a slightly smaller α value, $\alpha_C < 2$, while for the Riemann derivative we have to use a slightly larger α value, $\alpha_R > 2$ and therefore using the Riemann fractional derivative definition implies the need for box normalization, if we want to generate the exact level spacing of rotational type.

The behavior of the eigen functions $\Psi_n^{\pm}(\xi, \alpha)$ differs significantly in the region $1 \leq \alpha \leq 2$ and $\alpha < 1$. In figure 3 we have plotted the occupation probability for the eigen function $\Psi_{n=11}^-(\xi, \alpha)$ for the Caputo and Riemann solution.

Introducing the modified position operator $\bar{\xi} = \theta(\xi)\xi$, its expectation value

$$\langle \bar{\xi} \rangle = \int_0^{\infty} d\xi_{R,C} \Psi_n^{\pm}(\xi, \alpha) \xi_{R,C} \Psi_n^{\pm}(\xi, \alpha)^* \quad (28)$$

yields the position information on the positive half-axis. This value is almost constant for $\alpha > 1$. For increasing α only the side maxima are changing from inside to outside and therefore mark a smooth transition from Hermite-type to Bessel-type polynomials.

In contrast for $\alpha < 1$, the position value tends very fast to zero which means, that the wave function becomes strongly located at the origin in this case.

As a consequence, the energy diagram for $\alpha < 1$ is dominated by the kinetic term, since for the potential near the origin

$$\lim_{\xi \rightarrow 0} |\xi|^{2\alpha} = 0 \quad (29)$$

holds.

This means, that the solutions of the fractional Schrödinger equation for the harmonic oscillator and the solutions for the free fractional Schrödinger equation more and more coincide for $\alpha < 1$, a behavior, which we expect for any potential, which vanishes at the origin.

The eigen functions of the free fractional Schrödinger equation are known analytically and are given in terms of the Mittag-Leffler functions $E_{\alpha}(z)$ and $E_{\alpha,\beta}(z)$ as:

$${}_C\Psi_n^{+free}(\xi, \alpha) = E_{2\alpha}(-\xi^{2\alpha}) \quad (30)$$

$${}_C\Psi_n^{-free}(\xi, \alpha) = \xi^{\alpha} E_{2\alpha, 1+\alpha}(-\xi^{2\alpha}) \quad (31)$$

$${}_R\Psi_n^{+free}(\xi, \alpha) = \xi^{\alpha-1} E_{2\alpha, \alpha}(-\xi^{2\alpha}) \quad (32)$$

$${}_R\Psi_n^{-free}(\xi, \alpha) = \xi^{2\alpha-1} E_{2\alpha, 2\alpha}(-\xi^{2\alpha}) \quad (33)$$

and the corresponding eigen values are determined in box-normalization from the zeros of these functions. For $\alpha < 1$

Table 2. Parameter sets for the standard rot-vib-model (34) in the first row [2] and for the proposed generalized fractional model (39) to determine the energy levels of H^{35}Cl . Finally the rms-error is given.

stan- dard	B_e 10.59341 $\hbar\omega_e$ 2990.946	α_e 0.30718 $\hbar\omega_e x_e$ 52.8186	D_e $5.3194 \cdot 10^{-4}$ $\hbar\omega_e y_e$ 0.2243	β_e $7.51 \cdot 10^{-6}$ rms-error 3.8%
WKB	\tilde{B}_e 7.406 α_J 1.997	$\tilde{\alpha}_e$ 0.202 α_ν 1.051	g_0 152.016	$\hbar\tilde{\omega}_e$ 2707.77 rms-error 3.3%
Cap	\tilde{B}_e 5.264 α_J 1.91	$\tilde{\alpha}_e$ 0.155 α_ν 0.914	g_0 -64.973	$\hbar\tilde{\omega}_e$ 2938.77 rms-error 3.8%
Rie	\tilde{B}_e 2.588 α_J 2.081	$\tilde{\alpha}_e$ 0.080 α_ν 0.937	g_0 10.355	$\hbar\tilde{\omega}_e$ 3095.36 rms-error 3.8%

there exists only a finite number of zeros and therefore the energy spectrum is limited [15].

In the upper row of figure 4 we show the lowest energy levels for the fractional harmonic oscillator for $\alpha < 1$. This spectrum is limited to a finite number of levels, which may now be understood in comparison to the plot of zeros of the solutions of the free fractional Schrödinger equation presented in the lower row of figure 4.

It can be deduced, that the onset of real eigenvalues for a given α of the fractional harmonic oscillator and the occurrence of a zero in the potential free solution agree qualitatively.

Since the free fractional Schrödinger equation is formally equivalent to the classical fractional harmonic oscillator differential equation we may conclude, that in the special case of the harmonic oscillator the transition from fractional classical mechanics to fractional quantum mechanics is smooth.

We have thus demonstrated, that the fractional quantum harmonic oscillator extends the symmetry of the standard harmonic oscillator and allows for a generalized description of rotational and vibrational degrees of freedom.

Since we want to emphasize this unifying point of view, an appropriate area of application is molecular spectroscopy, where an interplay between vibrations and rotations is observed.

Therefore we will investigate the properties of infrared spectra of diatomic molecules in the next section using the fractional quantum harmonic oscillator.

6 Application: The infrared-spectrum of H^{35}Cl

Traditionally diatomic molecules are treated in lowest order as rigid rotors with a fixed bond length, which in addi-

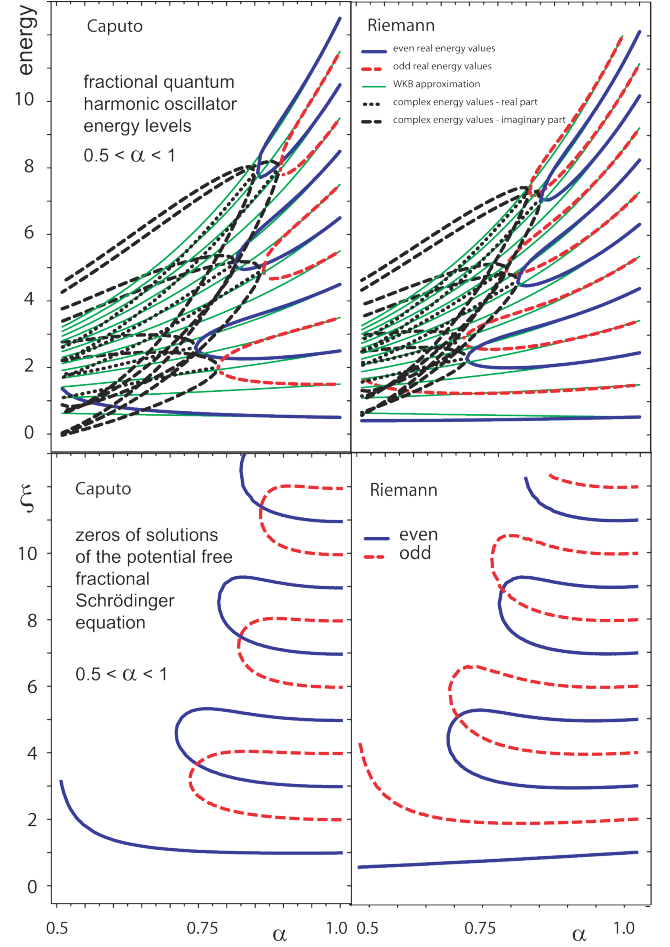


Fig. 4. In the upper row energy levels in the range $0.5 < \alpha < 1$ for the Caputo (left column) and Riemann (right column) fractional quantum harmonic oscillator are plotted. Blue lines indicate positive parity, dashed red lines indicate odd parity of the corresponding solution. For decreasing α , the number of real eigenvalues is reduced and are replaced by a conjugated pair of complex eigen values, dotted lines show the real part $Re(E)$ and dashed lines the complex $Re(E) \pm Im(E)$. Green lines show the WKB-approximation E_{WKB} . The lower row shows the zeros of eigen functions for the potential free fractional Schrödinger equation.

tion are able to perform vibrations around this equilibrium position.

For higher excitations, anharmonic contributions and the influence of centrifugal stretching are taken into account via a series expansion, which we present here up to third order:

$$E_{\text{rot-vib}}(\nu, J) = E_{\text{rot}} + E_{\text{vib}} = B_\nu J(J+1) + D_\nu J^2(J+1)^2 + \hbar\omega_e\left(\nu + \frac{1}{2}\right) + \hbar\omega_e x_e\left(\nu + \frac{1}{2}\right)^2 + \hbar\omega_e y_e\left(\nu + \frac{1}{2}\right)^3 \quad (34)$$

where the constants B_ν and D_ν add a rot-vib coupling via:

$$B_\nu = B_e - \alpha_e(\nu + \frac{1}{2}) \quad (35)$$

$$D_\nu = D_e - \beta_e(\nu + \frac{1}{2}) \quad (36)$$

which results in a seven parameter energy formula to determine the energy levels in the rot-vib model.

Now we introduce the fractional quantum harmonic oscillator model, which describes rotational and vibrational spectra from a unifying point of view. As we pointed out in the previous section, depending on the value of the fractional derivative parameter α we may generate both types of spectra:

$$E_{\text{rot}}(J) = E(\alpha \approx 2, J) \quad (37)$$

$$E_{\text{vib}}(\nu) = E(\alpha \approx 1, \nu) \quad (38)$$

Thus we propose the fractional analogue of the standard rot-vib-model:

$$\begin{aligned} E_{\text{rot-vib}}^{\text{fractional}}(\nu, J) = \\ E_{\text{rot}} + E_{\text{vib}} + E_{\text{coupling}} = \\ \tilde{B}_e E(\alpha_J \approx 2, J) + \hbar\tilde{\omega}_e E(\alpha_\nu \approx 1, \nu) + \\ \tilde{\alpha}_e E(\alpha_J \approx 2, J) E(\alpha_\nu \approx 1, \nu) + g_0 \end{aligned} \quad (39)$$

with six parameters α_J , \tilde{B}_e , α_ν , $\hbar\tilde{\omega}_e$, $\tilde{\alpha}_e$, g_0 . A least square fit of the fractional rot-vib model energies with the standard rot-vib model energies yields the parameter sets listed in table 2.

In order to emphasize the property of the fractional rot-vib model to realize rotational type spectra, we want to explore the lowest energy photon absorption processes in the infrared region. In that case from $\Delta J = \pm 1$, we obtain two branches (R and P) with the properties:

$$\Delta E_R(J) = E(\nu = 1, J + 1) - E(\nu = 0, J) \quad J = 0, \dots \quad (40)$$

$$\Delta E_P(J) = E(\nu = 1, J - 1) - E(\nu = 0, J) \quad J = 1, \dots \quad (41)$$

These transition energies may be directly compared to the experimental spectrum. The corresponding intensities I_j for a given transition are determined in the standard case by the Boltzmann-distribution

$$I_j = (2J + 1)e^{-E_{\text{rot}}/kT} = (2J + 1)e^{-B_\nu J(J+1)/kT} \quad (42)$$

where k is the Boltzmann constant. The factor $(2J + 1)$ is a result of the multiplicity of a given rotational state. In the case of the fractional rot-vib model this implies the following generalization:

$$I_j^{\text{fractional}} = (2(\alpha_J - 1)J + 1)e^{-E_{\text{rot}}/kT} \quad (43)$$

where the factor $(2(\alpha - 1)J + 1)$ now may be interpreted physically as a smooth transition of multiplicities from 1 to $2J + 1$ in the range $1 \leq \alpha \leq 2$, which means the transition from $U(1)$ to $SO(3)$. This may be interpreted as an indication for the connection of fractal space dimensions and fractional calculus.

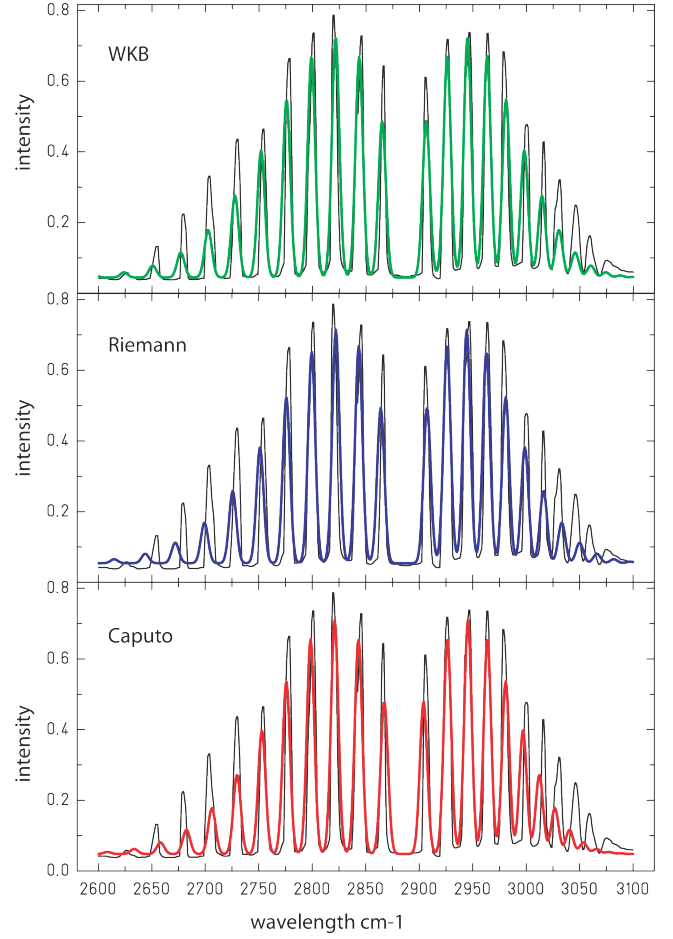


Fig. 5. Fit results for the infrared spectrum of H^{35}Cl in the wavelength range from 2600-3100 $[\text{cm}^{-1}]$. Black lines are the experimental values from [16]. From top to bottom the result for the energy levels of the fractional rot-vib-model (39) using the WKB-approximation, the Riemann and the Caputo fractional derivative definition.

With intensities (43) and assuming an exponential distribution for every transition we are able to fit the experimental spectrum [16]. The results are presented in figure 5.

The overall error is less than 4%. As a remarkable fact, the experimental spectrum is reproduced in the case of the Riemann fractional harmonic oscillator with $\alpha_J > 2$, which means, the corresponding eigen functions are only box-normalizable. Consequently, only the Caputo fractional rot-vib model describes the experiment within the allowed parameter range.

It is remarkable, that in the case of the fractional rigid rotor [17], which is an alternative description of rot-vib systems, just the opposite conclusion was drawn: the Caputo derivative based version was discarded and the Riemann rotor model was successful.

7 Conclusion and outlook

It has been demonstrated, that the fractional quantum harmonic oscillator generates an energy spectrum, which, besides vibrational degrees of freedom also shows rotational type spectra. The fractional parameter α allows for a smooth transition between these two extreme cases.

Therefore vibrations and rotations may be treated equivalently in a unified generalized rot-vib model, which may be successfully used to reproduce the infrared spectra of diatomic molecules, which has been demonstrated for the case of hydrogen chloride.

It has also been shown, that the WKB-approximation is a useful tool to approximate higher energy levels, but in the low energy region the exact solutions using the Riemann and Caputo derivative definitions differ significantly and cover a much broader area of useful applications.

In this paper we presented first results for the fractional quantum harmonic oscillator. The results encourage further studies in this field, especially the knowledge of eigen values and eigen functions for higher energy levels [18] will be useful to describe highly excited rotational molecular states, an area, which has been made accessible recently, see e.g. [19].

8 Acknowledgment

We thank A. Friedrich and G. Plunien from Technische Universität Dresden, Germany for useful discussions.

References

- Huygens, C. (1673). *Horologium oscillatorium sive de motu pendulorum ad horologia aptato demonstrationes geometricae* F. Muguet, Paris, France
- Herzberg, G. (1951). *Molecular spectra and molecular structure I: structure of diatomic molecules* 2nd Ed., D. Van Nostrand Company, New York, NY, USA
- Oldham, K. B. and Spanier, J. (1976) *The fractional calculus*, Dover Publications, Mineola, New York
- Podlubny, I. (1999) *Fractional differential equations*, Academic Press, New York
- Herrmann, R. (2011) *Fractional calculus - an introduction for physicists*, World Scientific Publishing, Singapore
- Riemann, B. (1847). *Versuch einer allgemeinen Auffassung der Integration und Differentiation* in: Weber H (Ed.), *Bernhard Riemann's gesammelte mathematische Werke und wissenschaftlicher Nachlass*, Dover Publications (1953), 353.
- Caputo, M. (1967) *Linear model of dissipation whose Q is almost frequency independent Part II* Geophys. J. R. Astr. Soc **13**, 529–539
- Dirac, P. A. M. (1930). *The principles of quantum mechanics* The Clarendon Press, Oxford
- Messiah, A. (1968). *Quantum mechanics* John Wiley & Sons, North-Holland Pub. Co, New York
- Feynman, R. P. (1949). *The theory of positrons* Phys. Rev. **76**, 749–759
- Weyl, H. (1927). *Quantenmechanik und Gruppentheorie* Z. Phys. **A46**, 1–46
- Parisi, G. and Wu, Y. (1981). *Perturbation theory without gauge fixing* Scientia Sinica **24**(4), 483–496, reprinted in Damgaard, P. H. and Hüffel, H. (Eds.) (1988). *Stochastic quantization* World Scientific Publishing, Singapore
- Laskin, N. (2002). *Fractional Schrödinger equation* Phys. Rev. E **66**, 056108–0561014
- Herrmann, R. (2007). *Common aspects of q -deformed Lie-algebras and fractional calculus* arXiv:0711.3701v1 [physics.gen-ph], arXiv:1007.1084v1 [physics.gen-ph], Physica A **389**(21), (2010) 4613–4622
- Hilfer, R. and Seybold, H. J. (2006). *Computation of the generalized Mittag-Leffler function and its inverse in the complex plane* Integral transforms and special functions **17**(9), 637–652
- National Institute of Standards and Technology (NIST) (2012). *Chemistry WebBook, NIST Standard Reference Database Number 69* <http://webbook.nist.gov/chemistry/>
- Herrmann, R. (2007) *The fractional symmetric rigid rotor* J. Phys. G: Nucl. Part. Phys. **34**, 607–25
- Herrmann, R. (2012) *Eigen values and eigen functions of the fractional quantum harmonic oscillator* Gam. Ori. Chron. Phys **1**, 1–588, accepted for publication
- Yuan, L., Teitelbaum, S. W., Robinson, A. and Mullin, A. S. (2011) *Dynamics of molecules in extreme rotational states* PNAS **108**(17), 6872–6877